Spectra of infrared transitions between highly excited states of polyatomic molecules

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It is shown that the average spectral characteristics of a highly excited polyatomic molecule (anharmonic shift, broadening, and integrated absorption cross section) can be determined from the constants of the vibrational spectra of low-lying levels. A study is made of the relationship between the intramolecular broadening of harmonic levels and the spectrum of IR transitions in a quasicontinuum of vibrational states. By way of illustration, a calculation is made for the ν_1 mode of a CF_3I molecule.

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1. INTRODUCTION

Studies of the vibrational states of polyatomic molecules are limited usually to the harmonic expansion of the Hamiltonian and to finding small anharmonic corrections by standard procedures of perturbation theory. Cases are encountered in which perturbation theory is inapplicable to some closely spaced levels of a molecule, i.e., levels experience a resonance and a direct diagonalization of the Hamiltonian has to be carried out. However, in the case of states of energy considerably greater than the average vibrational quantum the situation changes radically. A strong rise of the density of the vibrational states has the effect that the anharmonic interaction overlaps many closely spaced levels. Consequently, strong mixing of the levels (stochastization of the vibrational motion) is possible and this may alter the structure of the spectrum of IR transitions, from single lines allowed in the harmonic approximation to a so-called vibrational quasicontinuum. The existence of quasicontinuous transitions from any level in the case of a sufficiently strong vibrational excitation has been confirmed very convincingly by numerous experiments involving multiphoton IR laser excitation of molecules.[1,2]

Clearly, the most important physical application of the multiphoton excitation of molecules is the experimental investigation of nonlinear quantum systems in which a transition from weak to strong excitation corresponds to conversion of linear motion into stochastic.[3] Recent experiments[4] have shown that the stochastic range of motion of nuclei in molecules makes a considerable contribution to the energy spectrum even below the dissociation threshold D is reached. For example, in the case of SF_6 molecules the lower energy limit of the stochastic range, naturally somewhat arbitrary, is $E_{st} \approx 4000\ \mathrm{cm}^{-1}$ and the dissociation energy is $D \approx 32\,000\ \mathrm{cm}^{-1}$, whereas in the case of CF_3I molecules we have $E_{st} \approx 6000\ \mathrm{cm}^{-1}$ and $D \approx 18\,500\ \mathrm{cm}^{-1}$.

It is at present hardly realistic to expect that detailed spectra of transitions from a fixed highly excited vibrational–rotational state can be determined experimentally. There are at least two fundamental difficulties. First, for the energies given above the characteristic separation between neighboring levels is considerably less than the Doppler spacing, and in the case of strongly excited molecules this separation is considerably less than the natural widths. Second, in real experiments we are dealing with a distribution in a gas over a large set of vibration–rotational levels. The published experimental results point to three characteristic features: 1) the vibrational modes remain individual in the spectra and this applies to IR linear absorption[5] and fluorescence spectra,[6] as well as to the Raman scattering spectra[7]; 2) the band spectra shift toward longer wavelengths and this is naturally due to the anharmonicity; 3) in spite of the preservation of the overall mode structure of the transitions, the spectra of the individual bands broaden. This aspect is quantitatively least informative and this is again due to the actual distribution between the levels.

Our aim is to treat theoretically these features and to develop a method which would enable us to estimate the cross sections of IR transitions, their frequency dependences, and the evolution of these transitions on increase in the vibrational energy. We shall assume that the key to the understanding of the spectra of transitions between highly excited vibrational states of a molecule is the pattern of its intermode resonances.[3] We shall illustrate this approach by considering CF_3I molecules and estimating the anharmonic interaction constants using the available spectral data.[8] We shall also mention another feasible way of determining the transition cross section to the vibrational quasicontinuum, which is essentially semiempirical because it is based on a comparison with the characteristics of the process of multiphoton excitation of molecules. This approach gives reasonable results which can be compared with the experiments carried out on the CF_3I (Ref. 9) and OsO_4 (Ref. 10) molecules. We shall conclude our paper by considering briefly the correspondence between the two proposed approaches.

It should be stressed that at present the published data are highly contradictory even in the case of the simplest of problems, which is a very rough (to an order of magnitude) estimate of the transition cross sections. In particular, some laser-chemical experiments are explained in Ref. 11 assuming an anomalously strong (by two orders of magnitude) increase in the cross section on increase in the vibrational energy. It is not surprising that such subtle aspect as the band

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profile is still subject to controversy. This will be discussed separately in Sec. 4.

2. HAMILTONIAN AND BASES EMPLOYED

Let N be the number of degrees of freedom of a molcule and let the first mode be infrared active with a transition spectrum that will be considered later. We shall write down the Hamiltonian in its standard form separating the harmonic terms from the anharmonic part that mixes the different coordinates:

$$\hat{H}=\hat{H}_0+\hat{H}_A, \quad \hat{H}_0=\sum_{i=1}^{N}\hat{H}_{0i}. \tag{1}$$

The oscillator functions that diagonalize the harmonic part will be denoted by $|v\rangle = |v_1 ... v_N\rangle$:

$$\hat{H}_0|v\rangle=\sum_{i=1}^{N}\nu_i(v_i+{}^1/_2)|v\rangle. \tag{2}$$

We shall be interested, in particular, in the form of the expansion in terms of a harmonic basis of "true" functions $|true\rangle = |t\rangle$ of the Hamiltonian $\hat{H}$:

$$\hat{H}|t\rangle=E_t|t\rangle, \quad |t\rangle=\sum_{v_1\ldots v_N}C^{t}_{v_1\ldots v_N}|v_1\ldots v_N\rangle. \tag{3}$$

We shall consider the dispersive nature of the coefficients $C^t_{v_1}...v_N$ as a function of the energy and we shall frequently speak of the "width" of a level $|t\rangle$ as a characteristic energy interval, so that levels $|v\rangle$ lying within this interval dominate the contribution to $|t\rangle$. To avoid terminological confusion, we shall stress particularly that this width is in no way related to any finite lifetime of the regular states (if the spontaneous decay is ignored, this time is naturally infinite). However, the width of a level $|t\rangle$ considered in a harmonic basis is most closely related to the observed widths in the spectrum of infrared transitions; this will be dealt with in later sections.

For the sake of convenience, we shall represent the anharmonic part $\hat{H}_A$ of Eq. (1) in the form of the sum

$$\hat{H}_A=\hat{H}_{A1}+\hat{H}_{AB}, \tag{4}$$

where the contribution $\hat{H}_{A1}$ contains terms that include the coordinate of the selected mode and all the other anharmonic interactions are included in $\hat{H}_{AB}$. We shall always speak of the first mode, bearing in mind that with a suitable change of notation the procedure employed can be applied to any mode. We can now rewrite the Hamiltonian in a form convenient for further operations:

$$\hat{H}=\hat{H}_{01}+\hat{H}_{A1}+\hat{H}(-1), \quad \hat{H}(-1)=\sum_{i=2}^{N}\hat{H}_{0i}+\hat{H}_{AB}, \tag{5}$$

i.e., we shall distinguish between two subsystems, the first mode ν_1 and the interacting $(N-1)$ vibrations, and write down part $\hat{H}_{A1}$ that mixes them.

The Hamiltonian $\hat{H}(-1)$ describes a "molecule" with a truncated number of the degrees of freedom. We can define the "semitrue" basis of states $|semitrue\rangle = |s\rangle$ which diagonalize this particular part of the total Hamiltonian:

$$\hat{H}(-1)|s\rangle=E_s|s\rangle, \quad |s\rangle=\sum_{v_2\ldots v_N}C^{s}_{i_2\ldots v_N}|v_2\ldots v_N\rangle. \tag{6}$$

The formulas in Eq. (6) are completely analogous to those *in* Eq. (3) if we bear in mind that the space of $|s\rangle$ is of lower dimensionality, but such a separation is highly convenient in, for example, further investigations of the behavior of an IR-active degree of freedom upon excitation.

In writing down the Hamiltonian we have been forced to use the averaged form. This has been done not only to achieve considerable simplification. There is a fundamental difficulty that it is not possible to find all the anharmonic Hamiltonian constants, because it is not the separate constants but a complex combination of them that determines the shifts and forbidden bands observed in the linear spectrum. If the average interaction constants can be varied independently, it is necessary to write down $\hat{H}_A$ separating the "natural" dependence on the frequencies and allowing for the symmetry properties of a molecule.

In the most general form, we can write down

$$\hat{H}_A=\sum_{ijk}V^{(3)}_{ijk}\hat{x}_i\hat{x}_j\hat{x}_k+\sum_{lmnp}V^{(4)}_{lmnp}\hat{x}_l\hat{x}_m\hat{x}_n\hat{x}_p+\ldots \tag{7}$$

We shall adopt two simplifications: first, we shall consider only resonances of the third and fourth orders. The illustrative calculation given below for a CF_3I molecule confirms that even allowance for the fourth-order resonances gives rise to a correction of just 10–20% compared with the procedure limited to the third order alone.

Second, instead of a set of constants $V^{(3)}_{ijk}$ and $V^{(4)}_{lmnp}$, we shall use two averaged constants V_3 and V_4, expanding the Hamiltonian in terms of the factors $\omega_i\hat{x}_i$ and retaining in the sum the scalar combinations for a given symmetry of the molecule, i.e.,

$$H_A=V_3\sum_{sim}\omega_i\omega_j\omega_k\hat{x}_i\hat{x}_j\hat{x}_k+V_4\sum_{sim}\omega_l\omega_m\omega_n\omega_p\hat{x}_l\hat{x}_m\hat{x}_n\hat{x}_p. \tag{8}$$

The sum in the above equation stands for combinations of coordinate products that are scalar in the symmetry group of the molecule. We can find them if we expand in terms of irreducible representations the direct product of the representations governing the coordinates occurring in a given term. The number of totally symmetric representations in this expansion determines the number of possible scalar combinations. In the case of equality of several indices in Eq. (8) we have to add a numerical factor which allows for the smaller number of such terms in Eq. (7).

3. AVERAGED CHARACTERISTICS OF A MOLECULAR SPECTRUM

Vibrational states in a quasicontinuum have been investigated employing two approaches. In one of them, developed directly in connection with experiments on multiphoton excitation of molecules, a pumped mode interacting with the field is considered.[12–14] The anharmonic interaction between modes is then allowed for by introducing times describing energy relaxation to a reservoir containing the other vibrational degrees of freedom. The other approach is not based on eigenstates of a molecule[14–17] and is of interest also in cases other than multiphoton excitation of molecules. In this approach many levels are found to be dipole-coupled.

We shall begin from eigenstates of a molecule as given by Eq. (3), and in the application of multiphoton excitation we shall formulate an intermediate approach when introduction of semitrue states of Eq. (6) makes it possible to avoid a phenomenological indeterminacy in the selection of relaxation times and yet to allow, in the determination of the absorption-line profile, for the existing correlation between the various states of the reservoir which differ only by a quantum of the excited mode.

A calculation of the exact values of the expansion coefficients $C^t_{v_1\ldots v_N}$ and $C^s_{v_1\ldots v_N}$ of Eqs. (3) and (6), containing the complete information on the eigenvalues and eigenfunctions of a molecule and of a "molecule" without one mode is unrealistic and often unnecessary. For example, in the case of an SF_6 molecule the energy of $10^4\ \mathrm{cm}^{-1}$ corresponds to a density of states $\sim 10^6\ \mathrm{cm}^{-1}$, whereas an experimental estimate states is 10–100 cm^{-1}. Therefore, the average parameters describing the form of smearing are of real interest. If we use sufficiently reliable experimental data (on the long-wavelength shift and broadening of the absorption spectra), the average parameters will include primarily the average anharmonic shift of a transition and the characteristic width of transitions to a vibrational quasicontinuum. Undoubtedly, both quantities exhibit dispersion, depending on the actual occupation numbers of the harmonic states contributing to the states $|t\rangle$ and $|s\rangle$.

As for the anharmonic shift, the determination of the zeroth approximation for the shift obtained using the anharmonicity constants is discussed in Refs. 9 and 10. The result of an absorption-spectrum shift that increases on increase of the energy is

$$\nu(E)=\nu_1+\frac{X_0E}{\nu_1},\quad X_0=\frac{1}{N}\sum X_{1i}\left(\frac{\nu_1}{\nu_i}\right)(1+\delta_{i1})g_i, \tag{9}$$

where the summation is carried out over all the modes and g_i is the degeneracy (the spectroscopic constants X_{1i} are chosen with allowance for their sign).

The most important is the problem of the information which can be obtained by representing the true wave functions of a molecule by a superposition of the states in the harmonic approximation. Since it is in the harmonic basis that the matrix elements of the dipole moment of transitions are simplest, it is clear that the expansion (3) is the simplest way to finding the IR spectrum. We have stressed already that in the case of real experiments the quantities of the greatest interest are the spectral characteristics averaged over many closely spaced true states. Naturally, the spectrum of transitions from a single state $|t\rangle$ differs from the average spectrum. However, this applies mainly to small-scale (in respect to frequency) fluctuations of the intensities of the individual lines and not to the profile of the band as a whole. What should be the qualitative form of the profile? So far, we only know that the profile is strongly dispersive. A more detailed discussion is given in Sec. 4, so that here we shall simply formulate the intermediate question: what is the form of the quantities $|C^t_{v_1\ldots v_N}|^2$ occurring in the expansion (3)?

First, it is clear that they also are of strongly dispersive nature, i.e., they are important at $E_t\approx\Sigma\nu_iv_i$. If this is so, we can introduce the concept of level width in a vibrational quasicontinuum as a characteristic energy interval of harmonic levels which dominate the contribution to $|t\rangle$. Within the width of this interval the harmonics are strongly mixed and this is ensured by the intermode interaction terms from the anharmonic part of the Hamiltonian.

Second, it is clear that the distant harmonic terms make a contribution to the true states which is given by perturbation theory (the criterion of distant and close states is governed by the value of the actual matrix element of the interaction). Therefore, we can make the case more specific by approximating the coefficient $|C^t_{v_1\ldots v_N}|^2$ with a Lorentzian profile and thus allow for the asymptotics in the wings and for the strong mixing of the close (within the required width) levels.

This Lorentzian-profile approximation is used widely in the literature,[18,19] and it is this approach which has provided an accurate description of the profile of an overtone observed in Refs. 20 and 21, while variation of the parameters of the Lorentzian profile in a semiempirical excitation model gave results in good agreement with experiments on multiphoton excitation of molecules.[9,10] Such a form relating two bases is known to be equivalent to exponential decay of a "prepared" harmonic state to true states (see, for example, Ref. 22).[1]

Finally, we obtain

$$[C^t_{v_1\ldots v_N}]^2\propto\left[\left(E_t-\sum\nu_iv_i-\Delta E_A\right)^2+\sigma_t^2(E_t)\right]^{-1}, \tag{10}$$

bearing in mind that the true form of the smearing has the same asymptotics and a characteristic anharmonically shifted maximum.

In the calculation of the broadening we note that the systematic contribution of the anharmonicity to the expression for the transition rates and the inequality $\Delta E_A\ll\nu_1$ in the case of a slower growth of the resultant broadening on increase in the energy will allow us later to ignore, for the sake of convenience, the regular anharmonic shifts and quantities such as ΔE_A.

Another natural simplification is obtained by using the concept of the average broadening $\sigma_t(E_t)$. All this reduces the problem to finding a one-parameter form of the expansion of the true functions in terms of $|v_1\ldots.v_N\rangle$. The above assumptions are sufficient for the determination of the broadening ocurring in Eq. (10). In fact, an exact calculation of all the terms from the Hamiltonian (8) gives the form (10). It is clear that if this diagonalization ignores only one anharmonic level $|i\rangle$ of energy E_i, then (because of the large number of the levels) the result is not affected. Therefore, we can now find the depth of a level $|i\rangle$ due to its "decay" to a vibrational quasicontinuum. Figure 1 shows the selected level $|i\rangle$ and the "smeared" harmonic state related to $|i\rangle$ by terms from the Hamiltonian (8). The broadening of level $|i\rangle$ is described, in accordance with the well-known formulas

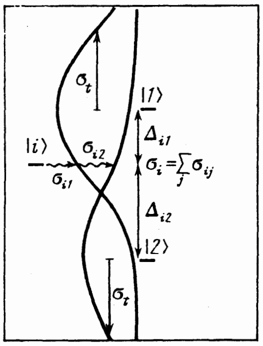

FIG. 1. Interaction of a selected harmonic state $|i\rangle$ with broadened harmonic states. By way of example, only two harmonic levels $|1\rangle$ and $|2\rangle$ are selected and these acquire a broadening σ_t because of the intermode anharmonicity. Here, Δ_{ij} is the defect of a resonance between harmonic states ($\Delta_{ij} = E_i - E_j$). The level $|i\rangle$ spreads into a quasicontinuous spectrum and acquires a width σ_i [See Eq. (13)].

for the rate of decay and for the existence of a quasicontinuous spectrum,[25] by the formula

$$\sigma_i = \sum_j \sigma_{ij}, \quad \sigma_{ij} = \frac{\langle i|\hat{H}_A|j\rangle^2 \sigma_t}{(E_i - E_j)^2 + \sigma_t^2}. \tag{11}$$

Here, $|i\rangle$ and $|j\rangle$ are the harmonic states, i.e., the difference $E_i - E_j$ between their energies is the known resonance defect. To use the term "decay" and consequently, Eq. (11), we must satisfy first the conditions

$$1/\rho_t^2 \leqslant \langle i|\hat{H}_A|j\rangle^2 \leqslant \sigma_t^2 + (E_i - E_j)^2. \tag{12}$$

Since the level $|i\rangle$ is in no way distinguishable, we can use Eq. (11) to obtain an equation for finding σ_t subject to the condition $\sigma_i = \sigma_t$. It should be noted that the reasonable assumption that the energy dependence of σ_t is weak, which is used in writing down the same values of σ_t for different $|j\rangle$ in Eq. (11), is supported by the results of a specific calculation, discussed below, for the CF_3I molecule. One further point: since we have decided to use averaged widths, the quantity σ_i should be averaged over many closely spaced levels. Finally, the problem has been reduced to an equation which is simple in the case of numerical calculations:

$$\sigma_t = \left\langle \sum_j \frac{\langle i|\hat{H}_A|j\rangle^2 \sigma_t}{(E_i - E_j)^2 + \sigma_t^2} \right\rangle_i. \tag{13}$$

It is worth stressing the self-consistent nature of Eq. (13). Beginning from the assumption of the possibility of the expansion (10), we have found the dacay width of a level (11) which is not distinguished in any way. It remains then to close the chain of reasoning by writing down Eq. (13).

A similar expression can be obtained also for a "molecule" without one mode [see Eq. (7)]:

$$[C^s_{v_2\ldots v_N}]^2 \propto \left[\left(E_s - \sum_{i=2}^{N} \nu_i v_i - \Delta E_A'\right)^2 + \sigma_s^2(E_s)\right]^{-1}, \tag{14}$$

where

$$\sigma_s = \left\langle \sum_j \frac{\langle i|\hat{H}_{AB}|j\rangle^2 \sigma_s}{(E_i - E_j)^2 + \sigma_s^2} \right\rangle_i.$$

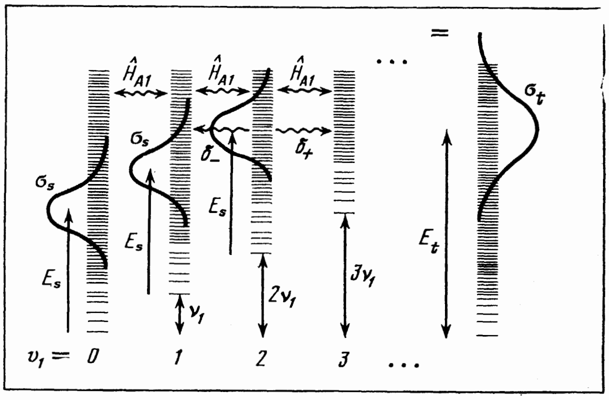

FIG. 2. Energy level scheme of a vibrational quasicontinuum. The energy level E_t is quasidegenerate. The harmonic approximation is used to separate the system into subcontinua differing in respect of the occupation numbers of the mode ν_1. In the presence of anharmonicity, which does not affect the mode ν_1, the levels in each quasicontinuum broaden (the width σ_s is independent of v_1). If the interaction $\hat{H}_{A1}$ for, the "semitrue" states become coupled and decay into neighboring subcontinua. The decay width of a semitrue state $\delta(E_t, v_1) = \delta_- + \delta_+$ [see Eq. (24)] denoted by σ_t represents the width of the "true" states when the energy is E_t.

We shall use the following notation: t and s are the indices referring to the discrete true and semitrue levels; ρ_t and ρ_s are the densities of states of a molecule and of a "molecule" without allowance for the mode ν_1; E_t and E_s are the corresponding energies. When summation over all the states is made, one can use the representation of the sum in the form of integrals with state densities ρ_t and ρ_s:

$$\sum_t f(E_t) = \int \rho(E_t) f(E_t)\, dE_t, \quad \sum_s f(E_s) = \int \rho(E_s) f(E_s)\, dE_s.$$

The use of Eqs. (13) and (14) allows us to check the correctness of the proposed procedure. In fact, we shall ignore the term $\hat{H}_{A1}$ in the Hamiltonian of the molecule. Then, the energy level scheme can be represented as shown in Fig. 2 without the terms giving rise to the interaction between the various subcontinua. All the levels $|t\rangle$ of energy E_t are obtained in the form of wave functions of the type

$$|v_1 = 0\rangle |s; E_s = E_t\rangle; \quad |v_1 = 1\rangle |s; E_s = E_t - \nu_1\rangle; \ldots \quad |v_1 = k\rangle |s; E_s = E_t - k\nu_1\rangle; \ldots \tag{15}$$

In the case of the level $|t\rangle$ we can determine σ_t from Eq. (13) and for each quasicontinuum we have $|v_1 = k\rangle |s$ and $E_s = E_t - k\nu_1$ in accordance with Eq. (14). (A change in the number of quanta of the first mode in the case of zero interaction $\hat{H}_{A1}$ does not alter the width!). A mutual agreement of the results can be obtained if

$$\rho_t(E_t)\sigma_t(E_t) = \rho_s(E_t)\sigma_s(E_t) + \rho_s(E_t - \nu_1)\sigma_s(E_t - \nu_1) + \ldots,$$

$$\hat{H}_{A1} = 0. \tag{16}$$

In the case of the example used below, Eq. *(16) is valid to* within 5–15% for all the energies ranging from the boundary of the stochastic region to the dissociation energy ($E_{st} \approx 6 \times 10^3\ \mathrm{cm}^{-1}$ and $D \approx 18.5 \times 10^3\ \mathrm{cm}^{-1}$ for CF_3I).

4. TRANSITIONS

The operator describing the interaction of a molecule with the radiation field is

$$\hat{\gamma}=\hat{\mu}E/2\hbar, \tag{17}$$

where $\hat{\mu}$ is the dipole-moment operator. The rate of absorption from a state E_t under the action of radiation of frequency Ω can be found in the standard way from the expression

$$W(E_t)=2\pi\overline{\gamma^2}\rho_t(E_t+\hbar\Omega). \tag{18}$$

In our case the operator $\hat{\gamma}$ acts only on the coordinates of the first mode and, therefore, in finding the matrix element of this operator it is convenient to expand the true states not as in Eq. (3) but so as to single out the mode ν_1. The wave functions $|v_1\rangle|s\rangle$ form a complete set in the space of vibrational coordinates of the whole molecule and, therefore, it is natural to use an expansion of the type

$$|t\rangle=\sum_{v_1,s}C^t_{v_1s}|v_1\rangle|s\rangle, \tag{19}$$

where the main contribution to the state $|t\rangle$ with an energy E_t is made by the wave functions $|v_1\rangle|s\rangle$ of energy $\nu_1v_1+E_s\approx E_t$. Therefore, Eq. (19) represents an expansion of the true states in terms of semitrue states, i.e., in terms of those states in which only the interaction $\hat{H}_{A1}$ is ignored. Obviously, if $\hat{H}_{A1}=0$, the coefficients $C^t_{v_1s}$ in Eq. (19) are given by

$$C^t_{v_1s}\propto\delta(E_t-\nu_1v_1-E_s),\quad \hat{H}_{A1}=0. \tag{20}$$

This is the main convenience of the use of the bases $|s\rangle$ and $|t\rangle$, i.e., the interaction which does not affect the mode ν_1 makes no contribution to the width of a transition.

We shall now turn to calculation of the matrix element in Eq. (18). The integrated value of the transition force constant (which is independent of the basis) is given by

$$\sum_{t'}\langle t'|\hat{\gamma}|t\rangle^2=\left(\frac{\mu_{01}E}{2\hbar}\right)^2\sum_{v_1}\frac{\rho_s(E_t-\nu_1v_1)}{\rho_t(E_t)}(v_1+1). \tag{21}$$

To continue the discussion we shall specify the nature of the expansions of the wave functions used:

$$|t\rangle=\left(\frac{\sigma_t(E_t)}{\pi\rho_t(E_t)}\right)^{1/2}\sum_{v_1\ldots v_N}\frac{(-1)^{t,v}}{[(E_t-E_v)^2+\sigma_t^2(E_t)]^{1/2}}|v_1\ldots v_N\rangle, \tag{22}$$

$$|s\rangle=\left(\frac{\sigma_s(E_s)}{\pi\rho_s(E_s)}\right)^{1/2}\sum_{v_2\ldots v_N}\frac{(-1)^{s,v}}{[(E_s-E_v)^2+\sigma_s^2(E_s)]^{1/2}}|v_2\ldots v_N\rangle, \tag{23}$$

$$|t\rangle=\sum_{v_1}\left(\frac{\delta(E_t,v_1)}{\pi\rho_t(E_t)}\right)^{1/2}\times\sum_s\frac{(-1)^{t,s}}{[(E_t-E_s-\nu_1v_1)^2+\delta^2(E_t,v_1)]^{1/2}}|v_1\rangle|s\rangle, \tag{24}$$

where notation of the type $(-1)^{t,v}$ is used for the phase factors (±1). The widths employed are not independent. In particular, substituting Eq. (23) in Eq. (24) and comparing with Eq. (22), we obtain the relationship

$$\delta(E_t,v_1)+\sigma_s(E_s)=\sigma_t(E_t),\qquad E_s+\nu_1v_1=E_t. \tag{25}$$

Naturally, the formula (25) should be valid, strictly speaking, only if one width is used for each of the levels (22)–(24). However, if we are interested only in averaged widths, Eq. (25) should reduce to

$$\sum_{v_1}\rho_s(E_s)[\delta(E_t,v_1)+\sigma_s(E_s)]=\rho_t(E_t)\sigma_t(E_t),$$

$$E_s+\nu_1v_1=E_t, \tag{26}$$

and this relationship should be checked in each specific calculation. Allowing for the regular anharmonic shift in the substitution of Eq. (24), we find that the matrix element becomes

$$\langle t'|\hat{\gamma}|t\rangle^2=\frac{\gamma_{01}^2}{\pi}\sum_{v_1}\frac{v_1+1}{\rho_t(E_t)\rho_t(E_{t'})}\times\frac{[\delta(E_t,v_1)+\delta(E_{t'},v_1+1)]\rho_s(E_t-\nu_1v_1)}{[E_{t'}-E_t-\nu(E_t)]^2+[\delta(E_t,v_1)+\delta(E_{t'},v_1+1)]^2}. \tag{27}$$

The main conclusion which follows from the above discussion is that the absorption spectrum is determined not by the widths of the true states when they are expanded in a harmonic basis but by decay widths of semitrue states. Figure 2 shows an energy level scheme illustrating the procedure of finding the states in a vibrational quasicontinuum. The decay is understood here to be the broadening of a level $|v_1\rangle|s\rangle$ because of its interaction via $\hat{H}_{A1}$ with other subcontinua $|v_1'\rangle|s'\rangle$.

It remains to find the widths $\delta(E_t,v_1)$. For example, let us assume that as a result of partial diagonalization we obtain semitrue states $|v_1\rangle|s\rangle$. Thus, for a fixed energy E_t of a molecule we have quasidegeneracy (Fig.2). We shall now consider a specific level $|v_1\rangle|s_0\rangle$ interacting with a quasicontinuous set of levels $|v_1-1\rangle|s'\rangle$. The square of the matrix element of this interaction can be written down introducing $V^2(v,\Delta)$ to denote the sum of the squares of matrix elements of $\hat{H}_{A1}$ between all the sublevels of the degenerate levels $v=(v_1\ldots v_N)$ and $v+\Delta=(v_1-1,v_2'\ldots v_N')$ where Δ is one of the resonances under discussion. Since in the case of summation with respect to v' we encounter nonzero values only for some (coupled by resonance to a level v) terms of the sum, we can go over to a summation over resonances Δ. If for a given Δ, we use the value averaged over the many states $V^2(v,\Delta)$, we then find that

$$\langle v_1s_0|\hat{H}_{A1}|v_1-1,s'\rangle^2=\frac{1}{\pi\rho_s(E_{s'})}\sum_\Delta\left\langle\frac{V^2(v,\Delta)}{g(v)}\right\rangle_v\times\frac{\sigma_s(E_{s_0})+\sigma_s(E_{s'})}{(E_{s'}-E_{s_0}-\nu_1+\Delta)^2+(\sigma_s(E_{s_0})+\sigma_s(E_{s'}))^2}, \tag{28}$$

where $g(v)$ represents degeneracy of the level v. If the decay width of a level $|v_1\rangle|s_0\rangle$ to a subcontinuum $|v_1-1\rangle|s'\rangle$ given by

$$\delta_-=\pi\rho_s(E_{s'})\overline{\langle v_1s_0|\hat{H}_{A1}|v_1-1,s'\rangle^2}$$

satisfies the inequality

$$\delta_- \leqslant \sigma_s + \Delta_i, \tag{29}$$

we can use the resonance approximation assuming that $E_{s'} = E_{s0} + \nu_1$. The decay to a subcontinuum $\delta(E_t, v_1)$ is found in the same way and also the condition on the decay width δ_+. Finally, the width $\delta(E_t, v_1)$ of Eq. (24) is found to be

$$\delta(E_t, v_1) = \delta_- + \delta_+ = \sum_\Delta \left\langle \frac{V^2(v,\Delta)}{g(v)} \right\rangle_v \times \frac{\sigma_s(E_t - \nu_1 v_1) + \sigma_s(E_t - \nu_1 v_1 + \nu_1)}{\Delta^2 + [\sigma_s(E_t - \nu_1 v_1) + \sigma_s(E_t - \nu_1 v_1 + \nu_1)]^2}$$
$$+ \sum_\Delta \left\langle \frac{V^2(v,\Delta)}{g(v)} \right\rangle_v \frac{\sigma_s(E_t - \nu_1 v_1) + \sigma_s(E_t - \nu_1 v_1 - \nu_1)}{\Delta^2 + [\sigma_s(E_t - \nu_1 v_1) + \sigma_s(E_t - \nu_1 v_1 - \nu_1)]^2}. \tag{30}$$

Here, the first term allows for resonances of the $(v_1 \ldots v_N)$ $(v_1 - 1 \ldots v'_N)$ type, and the second for resonances $(v_1 \ldots v_N) \to (v_1 + 1 \ldots v'_N)$. Then,

$$\delta_+(E_t, v_1) = \frac{\rho_s(E_t - \nu_1 v_1 - \nu_1)}{\rho_s(E_t - \nu_1 v_1)} \delta_-(E_t, v_1 + 1).$$

5. EXAMPLE OF A CF_3I MOLECULE

We shall now give the results of a numerical calculation for a CF_3I molecule. We shall estimate the constants V_3 and V_4 using the results of Ref. 8 reporting an investigation of the band shifts and of the forbidden bands of this molecule. The constants f_{123} and X_{12} given in Ref. 8 can be used to estimate

$$f_{123} = (\omega_1 \omega_2 \omega_3)^{1/2} V_3 / 8^{1/2} = 8.2 \text{ cm}^{-1}, \quad V_3 = 1.5 \cdot 10^{-3} \text{ cm}^{1/2},$$
$$X_{12} = \omega_1 \omega_2 V_4 / 4 = 1 \text{ cm}^{-1}, \quad V_4 = 0.5 \cdot 10^{-5} \text{ cm}. \tag{31}$$

The normalization factors are selected in accordance with the general formula for the Hamiltonian (8) and for the matrix elements of the coordinates in the harmonic basis.

We must stress here the illustrative nature of the calculation designed to determine the orders of magnitude of the cross section and the dependences of the levels widths on the energy of a molecule. Naturally, estimates made using other anharmonic constants can give other values of V_3 and V_4 so that the question of the correct average interaction constants has not yet been answered.

In writing down the Hamiltonian (8) we have confined ourselves to the terms corresponding to resonance defects up to 200 cm^{-1}. Allowing for the symmetry of the molecule (C_{3v}), we find there are 10 such resonances of the third order and 32 of the fourth order. The molecular frequencies were also taken from Ref. 8. All the terms of the Hamiltonian were written down in scalar combinations in the group C_{3v} and for these it was easy to determine the sums of the squares of the matrix elements of the interaction between the sublevels coupled by a resonance between the levels. We shall not give the table of resonances or details of the calculations. These calculations are easily reproduced using the values of the frequencies and the known symmetry properties.

Figure 3 gives a plot of the level widths in the quasicontinuum. We can see that they become considerable, amounting to several hundreds of reciprocal centimeters. The power-law dependence of the level of the energy can be represented in the form $\sigma(E) \propto E^{1.6}$. This is naturally explained by the order of the resonances under discussion (see also the Conclusion).

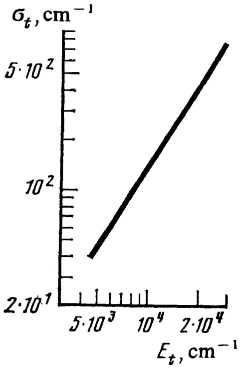

FIG. 3. Illustrative example of a CF_3I molecule. The level widths in the quasicontinuum are shown as a function of the energy of vibrational excitation. $V_3 = 1.5 \times 10^{-3}$ cm$^{1/2}$, $V_4 = 0.5 \times 10^{-5}$ cm.

In finding the average level width it is easy to calculate also the dispersion, which ranges from 50% for energies $E \approx 5 \times 10^3$ cm^{-1} to 25% for $E \approx 25 \times 10^3$ cm^{-1}. However, the influence of such a large deviation from the average value may not be observed in real experiments when the source emits a line of finite width.

Figure 4 gives, for a fixed total molecule energy E_t, the broadenings of the semitrue levels $\sigma_s(E_s)$ and the corresponding decay widths to the adjacent quasicontinua (i.e., $v_1, E_s \to v_1 + 1, E_s - \nu_1$ and $v_1, E_s \to v_1 + 1, E_s + \nu_1$). Figure 4 also shows a plot of the sum $\sigma_s(E_s) + \delta(E_{ts} v_1)$. We can see that for the majority of subcontinua with different values of v_1 the relationships of Eq. (25) are satisfied, though this is not self-evident. Moreover, we can easily imagine a situation when this is not true. For example, if $\hat{H}_{A1} = 0$, then $\delta = 0$. As pointed out earlier, we can in general expect Eq. (26) to be satisfied and this provides a check on the calculation method. Clearly, Eq. (25) follows from Eq. (26) so that the conditions

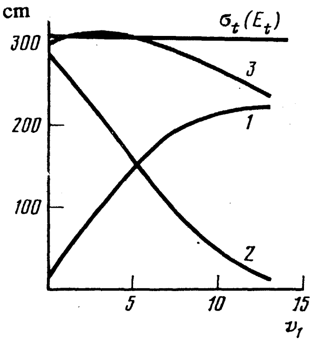

FIG. 4. Illustrative example of a CF_3I molecule. The decay widths $\delta(E_t, v_1)$ of the subcontinuum (1) with different occupation numbers v_1. Broadening of "semitrue" levels σ_s (2) with increase in the energy $E_s = E_t - \nu_1 v_1$. The excitation energy of the molecules in $E_t = 16.6 \times 10^3$ cm^{-1}. Curve 3 represents the sum $\sigma_s(E_s) + \delta(E_t, v_1)$.

$$\sigma_s(E_s)+\delta(E_t, v_1)=\sigma_t(E_t),$$
$$E_s+\nu_1 v_1=E_t$$

make it much easier to calculate the levels widths δ from the relations $\delta(E_t, v_1) = \sigma_t(E_t) - \sigma_s(E_s)$, rather than from the cumbersome formulas in Eq. (30).

Equation (25) can now be used even though it no longer holds for large values of v_1 (Fig. 4). This is because these terms make a negligible contribution to the cross sections of the transitions of Eq. (27) due to a rapid fall of the density $\rho_s(E_t - \nu_1 v_1)$ on increase in v_1. Physically, this is equivalent to the fact that the majority of states near the energy E_t have occupation numbers of the mode ν_1 close to the average value and not $v_{\max} \sim E_t/\nu_1$.

The same fact makes unimportant the deviation from inequality (29), which has to be satisfied in the calculation of the decay curves. This condition may be violated again only for the mode occupation numbers for those harmonic states with a given energy whose number is relatively small.

We shall now consider the profile of an absorption line and the energy dependence of the characteristic width. The formula (27) is a sum of several Lorentzian profiles and it is difficult to obtain an analytic expression for the effective width. However, in the far wing of the absorption line the relation (34) naturally gives the same asymptotic behavior as the Lorentzian profile. Introducing δ_{wing} for the width of a Lorentzian distribution which ensures this behavior, we find that the calculations yield

$$\delta_{wing}(10^4\text{cm}^{-1})\approx 110\,\text{cm}^{-1},\quad \delta_{wing}(2\cdot 10^4\,\text{cm}^{-1})\approx 270\ \text{cm}^{-1}. \tag{32}$$

The true line profile (Fig. 5) is characterized by a somewhat narrower intensity distribution than that given by a Lorentzian curve the given widths. However, in estimates we can assume that

$$\delta_{wing}\propto E^{1,3}. \tag{33}$$

If we introduce the half-width at midamplitude for the absorption cross section (27), we find that

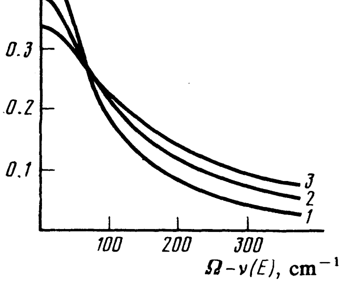

FIG. 5. Illustrative example of a CF$_3$I molecule. Behavior of the absorption cross section in the quasicontinuum: 1) $E = 11.2\times 10^3$ cm^{-1}; 2) $E = 16.6\times 10^3$ cm^{-1}; 3) $E = 22\times 10^3$ cm^{-1}. The curves are symmetric relative to the frequency $\nu(E)$ and $\Omega = 10^3$ cm^{-1}.

$$\delta_{1/2}(10^4\ \text{cm}^{-1})\approx 70\ \text{cm}^{-1},$$
$$\delta_{1/2}(2\cdot 10^4\ \text{cm}^{-1})\approx 140\ \text{cm}^{-1}. \tag{34}$$

Calculations indicate that the energy dependence of this characteristic transition width is linear.

6. CONCLUSION

We shall now try to establish the relationship between the calculated values and those found in a specific experiment. The concept of the average width of smearing of harmonic states in the formation of eigenlevels of a vibrational Hamiltonian (vibrational quasicontinuum levels) has made it possible to represent in a simple form the true wave functions as expansions in harmonic functions. Therefore, all the observed characteristics—provided only that they are not related to the interference between the various terms in Eq. (3)—can be calculated by the procedure described above. In particular, the linear absorption spectrum in the vibrational quasicontinuum range for a group of states of energy E_t is described by Eq. (27). Therefore, when the procedure is applied to experiments on multiphoton excitation of molecules, it can be used to calculate the rates of excitation in the vibrational quasicontinuum region and to give explicitly the kinetic equations whose solutions (see Refs. 1 and 2) give such observable characteristics as the absorbed energy, dissociation yield, etc., for molecules excited to the stochastic range.

The results of our investigation have drawn attention to two principal aspects: 1) the feasibility of calculating the average widths of vibrational quasicontinuum levels using constants that can be deduced by standard spectroscopy [Eq. (13)]; 2) the complex relationship between the widths of the absorption spectra and the characteristic broadening of the harmonic levels σ_t [Eqs. (27) and (30)]. The latter is confirmed by the following trivial example. Let us consider a molecule for which the anharmonic part of the Hamiltonian does not contain the coordinates of an infrared-active mode. Then, the majority of levels in the harmonic approximation is undoubtedly mixed and the true energy spectrum of the molecule can be very far from harmonic. However, the absorption spectrum is δ-like for an initial distribution of the populations (naturally, without allowance for the notational width). In other words, if the matrix element $\langle t'|\hat{\gamma}|t\rangle^2$ is found using Eq. (22), the cross terms cancel the diagonal terms and the result has the form of Eq. (20). This limiting case ($\delta = 0$ when $\hat{H}_{A1} = 0$) is also included in our analysis in a natural way.

It should be pointed out that the whole procedure of the calculation widths given above is explicitly based on the assumption that in writing down the anharmonic part of the Hamiltonian we can confine ourselves to the third- and fourth-order terms. The validity of this assumption in our case in confirmed by the small contribution to the result of even the terms of the fourth order compared with the third, but this must be justified in each specific case.

Our example of the ν_1 mode of a CF$_3$I molecule is sufficiently "average" i.e., the simpler relationships (25) are applicable to it, but this cannot be expected in the most general case. The degree to which the characteristics of formation of the transition spectra are manifested in each specific case can be found only by considering the specific pattern of intermode resonances.

The following comments can be made about the irregular ("accidental") frequency dependence of the cross section in the case of excitation in a vibrational quasicontinuum. In fact, if we assume that an isolated high vibrational–rotational state can be excited we should find that in the case of an infinitely narrow line there should be abrupt jumps of the absorption between neighboring transitions and the relative dispersion should be ~ 1. However, we are always dealing with a source of finite width $\Delta\nu$ so that we always excite simultaneously many states $[n \approx \rho(E)\Delta\nu]$. An obvious estimate then gives the relative dispersion of the absorption cross section as $\sim 1/\sqrt{n}$. Therefore, in real experiments we cannot expect an abrupt irregular frequency dependence.

The energy dependence of the broadening in a vibrational quasicontinuum points to an obvious fact. The dependences of the widths of harmonic levels in the formation of true eigenstates obtained in the case of CF_3I ($\sigma \propto E^{1.6}$), are self-evident from the following physical considerations. In the case of the third order resonances which govern mainly the widths in the example under discussion we can expect the dependence $\sigma \propto E^{3/2}$ because of an increase in the harmonic matrix element of each of the terms $\hat{x}_i\hat{x}_j\hat{x}_k$ on increase in the energy. This is the dependence assumed in Ref. 9 in deriving a semiempirical model of multiphoton excitation of CF_3I. However, an estimate obtained for the widths (33) of the transition lines gives a somewhat weaker dependence. This must be allowed for in considering other specific examples. However, it should be pointed out that in a comparison with the experimental results our clculations were purely illustrative) we must determine more accurately the average constants of the V_3 and V_4 type or, possibly, vary them independently and this should naturally affect the energy dependence of the cross sections.

The procedure proposed above for the calculation of the average widths (13) is essentially the zeroth approximation for further iteration in the determination of the widths of specific levels. However, in many situations it is sufficient to know the average value and it is diffucult to obtain higher approximations, so that the above method may be sufficient. The authors are grateful to V. S. Letokhov for his interest and to V. N. Sazonov for valuable comments.

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[1] One should point out the treatments in Refs. 23 and 24, where non-Lorentzian profiles are obtained for these transitions. However, in these treatments an allowance has been only made for the intramode anharmonicity, or the discussion has been limited to just one intermode resonance.

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